

(19)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets

(11) Publication number:

**0 227 197**  
**A2**

(12)

# EUROPEAN PATENT APPLICATION

(21) Application number: 86202366.0

(51) Int. Cl. 4: C10J 3/54

(22) Date of filing: 23.12.86

(30) Priority: 27.12.85 US 813735

(43) Date of publication of application:  
01.07.87 Bulletin 87/27(94) Designated Contracting States:  
DE GB IT NL

(71) Applicant: SHELL INTERNATIONALE  
RESEARCH MAATSCHAPPIJ B.V.  
Carel van Bylandtlaan 30  
NL-2596 HR Den Haag(NL)

(72) Inventor: Hardesty, Donald Ernest  
2210 Creek Road  
Brookshire Texas 77423(US)

(74) Representative: Aalbers, Onno et al  
P.O. Box 302  
NL-2501 CH The Hague(NL)

(54) Oxidation of char and slag.

(57) A process for the partial combustion or oxidation of coal is described, the process being characterized by recovery of energy value in gasification zone bottom impurity solids (e.g. char) and concomitant reduction of solids disposal requirements. In particular, the char is oxidized in a fluidized bed, preferably with other carbonaceous materials, and the heat recovered is used, e.g., to dry feed coal.

EP 0 227 197 A2

## OXIDATION OF CHAR AND SLAG

The invention relates to a process for the gasification of coal to produce synthesis gas comprising the steps of feeding particulate coal to a gasification zone, and partially oxidizing coal with oxygen in said gasification zone, producing a gas stream comprising synthesis gas, and impurity materials which are collected in a water bath as char, fine slag, and coarse slag; removing a material comprising char from said water bath.

Usually in processes for the gasification of coal to produce synthesis gas, significant quantities of unreacted impurity matter, variously referred to as char and slag, are produced during combustion or oxidation in the gasification zone. Upon separation of the char and/or slag from the gasification zone, a disposal problem exists, since these materials have undesirable properties which limit options for their disposal. At the same time, the char, and at least some of the fine slag, contains, in addition to mineral matter or components, a residual carbon content that has significant energy value. For example, the char and fine slag may contain from about 5 per cent to about 90 per cent by weight carbon, based on the total weight of the char and fine slag. If the char, or char and fine slag are disposed of, e.g., as land fill, this energy value is lost. Accordingly, a procedure which captured this energy value, at the same time reducing the volume of material to be disposed of, could have economic importance. The invention provides such a procedure.

Additionally, if coal is dried to remove the bulk of the moisture therein before gasification, the removal of this moisture involves a significant energy expenditure. If coal is combusted to provide the heat necessary for the drying, from about 2 per cent to about 12 per cent by weight of the total coal supplied to the process may be utilized, thus lowering the efficiency of the process. The invention, in a further embodiment, is directed to reducing this energy expenditure.

A process for gasification of coal characterized by utilization of heat values obtained from flyash, with concomitant reduction of material for disposal has already been proposed. The present invention is complementary thereto, such that a common fluidized bed oxidation zone for heat energy recovery may be employed.

Therefore, it is an object of the invention to provide a process for the partial oxidation or combustion of coal in which disposal problems for the char and fine slag are reduced, and energy costs

for the process are reduced. The invention, further, combines a procedure for reducing char and fine slag disposal with a coal drying procedure, so that improvement in both techniques is achieved.

Therefore, the process of the invention is characterized by the steps of fluidizing removed char in a fluidized bed in a fluidization zone, and oxidizing said char in said fluidized bed with oxygen at a temperature below the fusion temperature of the mineral components of the char and the bed, producing a substantially carbon-free residue and heated gases, and utilizing the heat in the heated gases. In an advantageous form, the invention comprises a process, as described, in which the partial oxidation or gasification is carried out in a gasification zone, the outlet temperature of which is from 1100 °C to 1800 °C, more advantageously 1200 °C to 1600 °C, and char separated - (advantageously, fine slag is also separated) is oxidized in a fluidized bed in a fluidization zone at a temperature of from 500 °C to 1150 °C, more advantageously 650 °C to about 1120 °C. Pressures in the gasification zone may be varied widely, but will advantageously range from 10 to 100 atmospheres, more advantageously from 20 to 50 atmospheres, while pressures in the fluidization zone will range from atmospheric to 10 atmospheres or higher. A rough separation of char and fine slag from coarse slag may be made in the gasification zone, or char and fine slag and all or a portion of the coarse slag may both be sent to the fluidization zone. As used herein, the term "char" refers to those materials, whether solid or molten, which remain in the gasifier upon production of synthesis gas, and have an average particle size - (on solidification, if molten) of less than 250 microns in width. "Fine slag" refers to those materials, whether solid or molten, which remain in the gasifier upon production of synthesis gas, and have an average particle size (on solidification, if molten) of greater than 250 microns, but less than 1 millimetre in size. As used herein, the term "coarse slag" refers to those materials which remain in the gasifier upon production of synthesis gas, and which have an average particle size upon solidification of greater than 1 millimetre in width. As indicated, char and fine slag contain varying portions of residual carbon, e.g., from 5 per cent by weight to 90 per cent by weight of residual carbon, based on the total weight of the char or fine slag, while coarse slag, which is generally a vitreous type of material, contains less than 1 per cent by weight of residual carbon.

Advantageously, the heat liberated may be used to generate steam or, the heat may be used to dry feed coal to the process. That is, in this embodiment, the invention relates to a process for the gasification of coal to produce synthesis gas in which particulate coal is dried in at least one drying zone, the coal is fed from at least one drying zone to a gasification zone, and partially oxidized or combusted, as hereinbefore described, to produce synthesis gas, char, fine slag, and coarse slag, which is treated as described, and the heat generated by oxidizing the char or char and fine slag is utilized in drying coal in at least one drying zone. As used herein, the term "oxygen", unless otherwise evident from the context where employed, is taken herein to include air, pure oxygen, air enriched with oxygen, and other oxygen-containing gases.

While the particular gasification or partial oxidation or combustion procedure employed is not per se part of the invention, the invention is particularly applicable to high pressure coal gasification slagging processes in which the coal is partially oxidized or combusted to produce, in addition to the synthesis gas, flyash, a bottom "char" material, fine slag and a vitreous or coarse slag which are collected in water bath in or associated with the gasification zone. The oxygen and coal flows are controlled so that little CO<sub>2</sub> is produced in the gaseous product. In general, these procedures are carried out by feeding coal, advantageously dry coal, e.g., coal having a moisture content of below about ten per cent by weight, entrained in a gas, such as an inert gas, into a gasification zone, and combusting or oxidizing the coal with oxygen. Flame temperatures may reach 3500 °C, with zone outlet temperatures advantageously from 1100 °C to 1800 °C. Pressures in these processes will range from 10 atmospheres to 100 atmospheres, advantageously from 20 atmospheres to 50 atmospheres. In one such process, the synthesis gas and flyash are removed from the upper portion of the gasification zone, and the char, fine slag, and coarse slag are collected from the lower portion in a water bath.

A wide variety of coals are suitable for use in the invention. For example, anthracite, bituminous coal, lignite, and so-called brown coal may be used in the invention. A real advantage of the invention is the ability to use lower grade coals, such as lignite. As used herein, the term "coal" is taken to include these inferior grade carbonaceous fuels, as well as the higher quality coals. The coal will advantageously be fed to the gasification zone in a particle size suitable for boiler furnace operation, e.g., 80 to 90 microns in diameter, although those skilled in the art may select the appropriate particle size, as desired. In an advantageous embodiment,

the invention is practised with "dry" coal, that is, coal having a moisture content of less than 10 per cent by weight, based on the weight of the moist coal.

Synthesis gas and entrained matter, which is known as, or becomes what is known as, flyash, is removed from the gasification zone and treated as described therein. Heavier solid particulate matter and molten matter remaining in the gasification zone are allowed to fall into the lower part of the reactor, and thence for example into a water bath, and are collected in the lower portion of the gasification zone. As those skilled in the art will recognize, a significant distinction between "flyash" and "char" is the density. Fine slag is somewhat denser, while coarse or vitreous slag has, as noted, little carbon content, and has a "glassy" appearance.

The char and fine slag may be separated roughly in the water bath by this density differential, although there will be some intermixture. That is, the coarse slag particles tend to fall to the bottom of the water bath, the fine slag above the coarse slag, and the char generally above the fine slag. Means, e.g., a sluice, may be provided for achieving the separation of the char, and fine slag, if desired, from the coarse slag. Alternately, all material may be removed, either intermittently or continuously, from the bottom or lower portion of the gasification zone water bath. It is thus not a requirement of the invention that the particles in question be separated in the gasification zone water bath; the portions may be separated by sizing equipment external to the bath. Moreover, it is within the concept of the invention that all of the "bottoms" material, i.e., char, fine slag, and coarse slag, be sent to the fluidization zone. If desired, the bottoms material may be crushed to ensure the desired size for fluidization.

According to the invention, at least the char, and advantageously the fine slag, are oxidized in a fluidization zone comprising at least one fluidized bed to remove the carbonaceous matter therein, producing a denser, more easily disposal of material. The heat liberated during oxidation may be captured by generation of steam, or may be used either directly or indirectly to dry the coal to be fed to the gasifier. As will be appreciated by those skilled in the art, the amount of heat generated from the bottoms material will be insufficient to dry the large volume of coal needed for the process. The bottoms material may be combined, as mentioned, with flyash, in the manner provided in the above-mentioned application. To supplement the heat generated by the bottoms material and flyash, other combustible or partially combustible materials or fuels, such as coal or coal fines, may be added

to the fluidized bed and oxidized. Obviously, a separate drying technique may also be used, but it is an advantage of the invention that an independent dryer or drying zone may be eliminated.

The type of fluidized bed or beds employed is a matter of choice. What is required, however, is that the bed or beds be operated at a temperature below the fusion temperature of the mineral matter in the bed, including that of a coal or fuel supplement. In general, the mineral content of flyash comprises silica, alumina, and other inorganic components in varying quantities, and the melting point of the mixture may be determined routinely. Since these temperatures are normally above 1482 °C - (although some may be less), problems with clogging will normally not be encountered if the bed is operated below this temperature. As indicated, the fusion temperature or range of temperatures may be determined routinely for each flyash or fuel utilized, and the temperature in the fluidized bed may be controlled accordingly. Advantageously, the temperatures are operated well below the fusion temperature, e.g., from 500 °C to 1150 °C, more advantageously from about 650 °C to about 1120 °C. Pressures in the fluidization zone may be varied to the extent suitable for fluidized beds, but may be ranged from atmospheric to 10 atmospheres, for example from atmospheric pressure to 5 atmospheres. The fluidized bed or beds may be jacketed, or may have coils to absorb the heat produced by the oxidation. The bed may contain other particulate matter, including catalysts. The combustion gases generated are removed from the fluidization zone, and transfer their heat, either directly or indirectly, as desired, advantageously to the coal feed. The coal can be ground and dried in a combination procedure, and to allow conventional equipment to be used, a moderating gas, such as air, or nitrogen, at a temperature of, for example, 15 °C to 40 °C, is added to the combustion gases to lower the temperature to 200 °C to 500 °C.

The invention will now be described in more detail by way of example with reference to the accompanying drawing, in which the figure is a schematic illustration of the process flow type showing an embodiment wherein the heat generated by oxidation of the bottoms material is used to dry feed coal. All values are calculated or exemplary.

Accordingly, reference numeral (1) designates a supply line from, for example, a storage vessel, not shown, in which coal having an average particle size diameter of 1.3 cm is fed to a drying zone (2) which contains a combination pulverizer-dryer wherein the coal is crushed to an average particle size of from 80 to 90 microns and dried by the gas stream in a line (3) to a moisture content of 10 per

cent by weight, based on the weight of the moisture and the coal. In this illustration, the gas stream in the line (3) has a temperature of 250 °C, contacts the coal directly in the combination pulverizer-dryer, and exits the drying zone (2) via a line (4). The exit gas may be treated for control of pollutants, or utilized (not shown). Concomitantly, dried particulate coal is removed from the drying zone (2) through a line (5) and forwarded to a gasifier (6). Means may be provided (not illustrated), for raising the pressure of the coal and entraining gas up to the level employed in the gasification zone. In the gasification zone (6), the coal is injected in an entraining gas, e.g. nitrogen, through nozzles and combusted in a reducing atmosphere or partially oxidized with pure oxygen at 25 atmospheres and at a flame temperature of 3400 °C to 3500 °C. Synthesis gas and impurity particles are removed overhead from the gasification zone at a temperature of 1400 °C, and sent to a quenching and cooling zone (7). Char and slag, which are heavier impurity materials, fall downward into the gasifier, and are removed from the lower portion thereof. The quench and cooling zone (7) can be connected directly to the outlet of the gasifier (6). The synthesis gas can be first quenched and cooled with cold recycle gas. The temperature of the synthesis gas can be lowered to 900 °C, and molten impurities in the gas are solidified to what is known as flyash. The quenching and cooling sequence can be carried out in more than one stage, the final temperature before separation of the flyash being from 235 °C to 320 °C.

In order to separate the flyash from the synthesis gas, the stream is forwarded via a line (8) to a cyclone (9) (or the cooling zone may discharge directly thereto). The great bulk of the flyash is separated in the cyclone (9), and the flyash is removed from the cyclone (9) via a line (10). The gas stream is removed from the cyclone (9) via a line (11) and sent for further processing, such as for H<sub>2</sub>S removal, and for product use. Because the cyclone is not totally effective, a final solids cleanup stage (12), e.g., bag filters, is provided in the line (11). Solids are removed from a unit (12) via a line (13). Solids from the cyclone (9) and the solids removal stage (12) may be utilized for energy recovery according to the invention.

The impurity molten materials and solids not removed with the synthesis gas from the reaction zone fall to the lower portion of the gasifier (6), and through a slag tap (20) into a water bath (21). Primarily because of differences in the density of the particles, a rough separation of the particles takes place, as mentioned previously. A sluice (22) is provided for removal of fine slag and char, and coarse slag may be removed from the bottom of

the bath at a line (23). The material separated in the sluice (22) is passed via a line (24) to a fluidization zone (14), wherein it is treated, as described hereinafter.

Accordingly, solids in the lines (10), (13) and (24) are injected into the fluidized bed (14), and are reacted with oxygen in excess from a line (15) at a temperature of 800 °C to 900 °C, which is well below the fusion temperature of the mineral components of the bed. The oxygen may serve as the fluidizing gas, or a separate fluidizing gas may be provided. The substantially carbon free residue may be removed via a line (16). Residence times of the solids will depend on the operating conditions, such as the temperatures, pressures, and specific equipment, and may be adjusted suitably by those skilled in the art. The combustion gas is removed from the bed (14) via the line (3), and is utilized as described previously. As noted previously, the total carbon present in the bottoms solids is insufficient to provide the required heat for drying the coal to the process. Normally, even the addition of flyash is not sufficient for this large requirement, and the flyash may be diverted for other purposes. To supplement the heat requirements, additional carbon-containing materials, such as coal fines, may be added to the fluidized bed (14) via a line - (25).

In order to determine if the bulk density of a sample of fine slag and char remaining from the gasification of coal might be increased, the sample was heated in a quartz dish for at least one hour in air at 750 °C in a muffle furnace. The sample weighed 69.11 grams and had a volume of about 82 ml. After the heat treatment, the sample weighed 61.2 grams, had a volume of about 55 ml. The loss on ignition was 11.4 per cent by weight, based on the weight of the original sample.

While the invention has been illustrated with particular apparatus, those skilled in the art will recognize that, except where indicated as material herein, other equivalent or analogous equipment may be employed. For example, crushing and drying equipment may be separate, and the gasifier need not have the specific configuration shown. Means other than a sluice may be provided for fine slag and char removal.

Again, as used herein, the term "zone", as employed in the specification and claims, includes, where suitable, the use of segmented equipment operated in series, or the division of one unit into multiple units to improve efficiency or overcome size constraints, etc. For example, a series of cyclones may be employed, and the quench and cooling operations are preferably carried out in multiple units, utilizing different techniques. Parallel

operation of units, is, of course, well within the scope of the invention, and all equipment, such as pumps, valves, control units, etc. has not been illustrated.

## Claims

1. A process for the gasification of coal to produce synthesis gas comprising the steps of feeding particulate coal to a gasification zone, and partially oxidizing coal with oxygen in said gasification zone, producing a gas stream comprising synthesis gas, and impurity materials which are collected in a water bath as char, fine slag, and coarse slag;

removing a material comprising char from said water bath; characterized by the steps of fluidizing removed char in a fluidized bed in a fluidization zone, and oxidizing said char in said fluidized bed with oxygen at a temperature below the fusion temperature of the mineral components of the char and the fluidized bed, producing a substantially carbon-free residue and heated gases, and utilizing the heat in the heated gases.

2. The process as claimed in claim 1 characterized in that fine slag is present in the material removed from the water bath, and the fine slag is fluidized and oxidized in the fluidized bed, the temperature employed also being below the fusion temperature of the mineral components of the fine slag.

3. The process as claimed in claim 1 characterized in that coarse slag is present in the material moved from the water bath, and the coarse slag is fluidized in the fluidized bed, the temperature employed also being below the fusion temperature of the mineral components of the slag.

4. The process as claimed in claim 2 characterized in that the temperature in the fluidized bed is maintained below about 1482 °C, but below the fusion temperature of the mineral components of the fluidized bed.

5. The process as claimed in claim 2 characterized in that the heat from the heated gases is used to generate steam.

6. The process as claimed in claim 2 characterized in that the heat is utilized by contacting the heated gases directly with moist coal to remove moisture from the coal.

7. The process as claimed in claim 1 characterized in that the heat is utilized by contacting the moist coal with a solid or gas heated directly or indirectly by said heated gases.

8. The process as claimed in any one of claims 1-7 comprising the steps of partially oxidizing coal with oxygen in said gasification zone at a pressure

of from 10 atmospheres to 100 atmospheres, the gasification zone outlet temperature being from 1100 °C to 1800 °C, characterized by the steps of oxidizing said char in said fluidized bed with oxygen at a temperature of from 500 °C to 1150 °C, but below the fusion temperature of the mineral components of the fluidized bed, and a pressure of about atmospheric or higher.

5

10

15

20

25

30

35

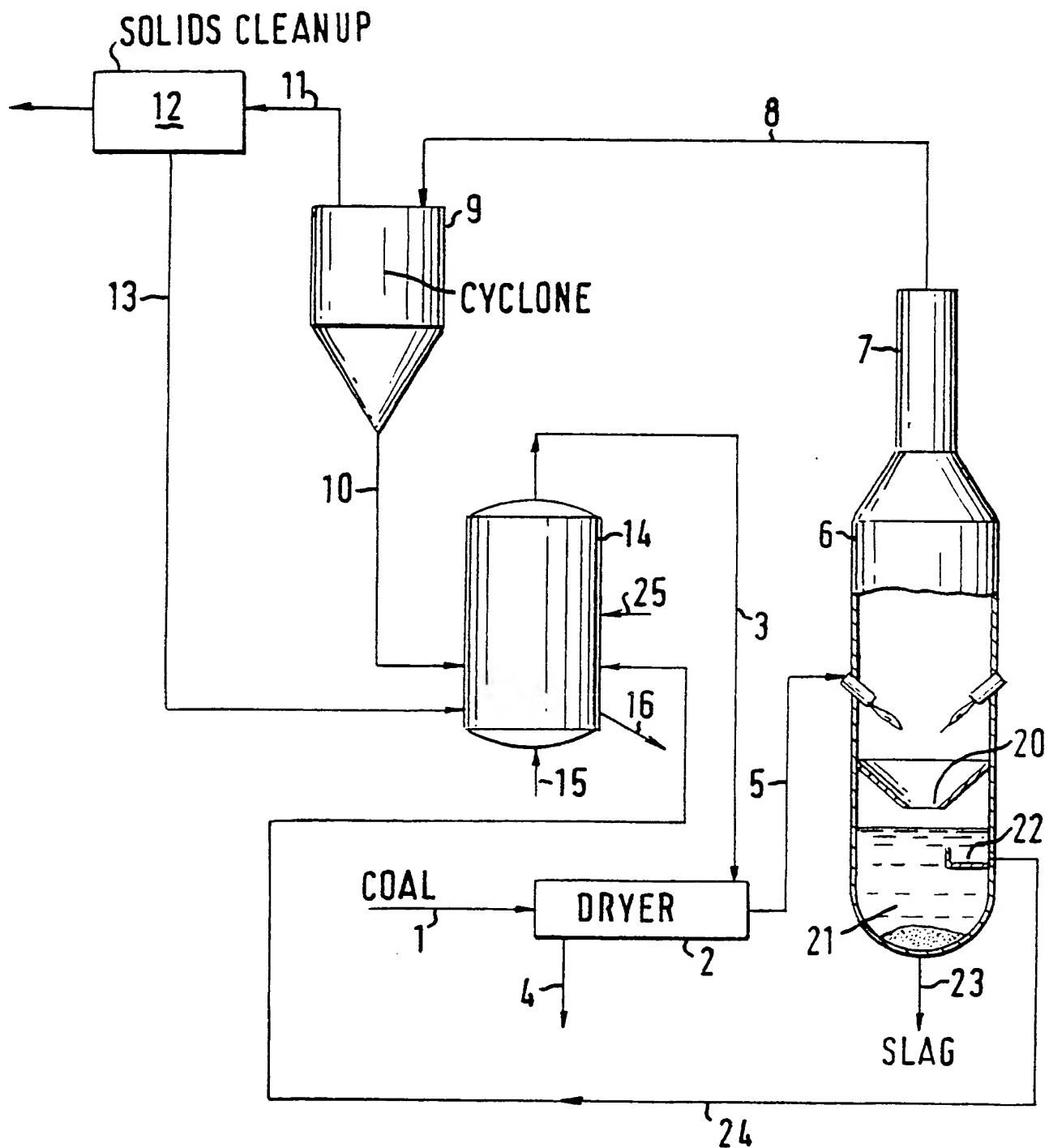
40

45

50

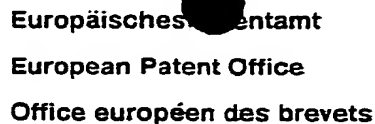
55

6









**0 227 197**  
**A3**

**EUROPEAN PATENT APPLICATION**

⑤ Int. Cl.4: **C10J 3/54**, C10J 3/84,  
C10J 3/46

② Date of filing: 23.12.86

71 Applicant: **SHELL INTERNATIONALE  
RESEARCH MAATSCHAPPIJ B.V.**  
Carel van Bylandtlaan 30  
NL-2596 HR Den Haag(NL)

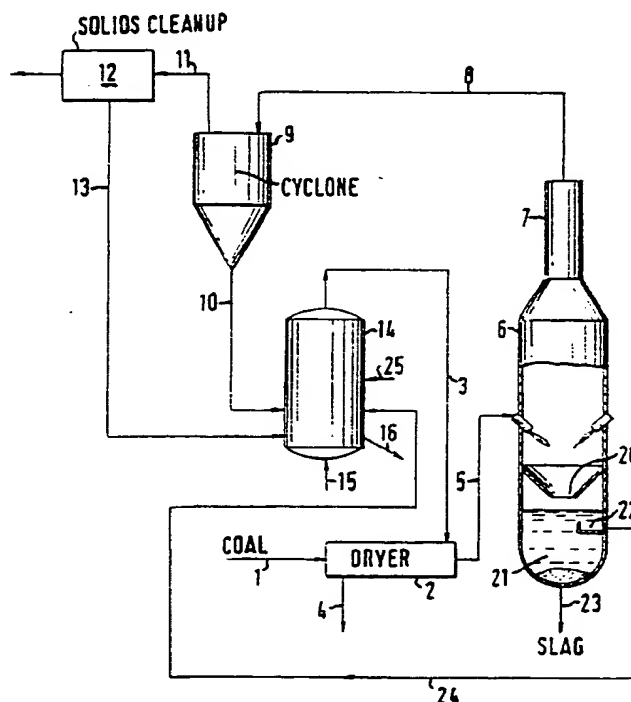
**(72) Inventor: Hardesty, Donald Ernest**  
**2210 Creek Road**  
**Brookshire Texas 77423(US)**

74 Representative: **Aalbers, Onno et al**  
**P.O. Box 302**  
**NL-2501 CH The Hague(NL)**

Ⓢ Date of deferred publication of the search report:  
27.01.88 Bulletin 88/04

**⑤④ Oxidation of char and slag.**

57) A process for the partial combustion or oxidation of coal is described, the process being characterized by recovery of energy value in gasification zone bottom impurity solids (e.g. char) and concomitant reduction of solids disposal requirements. In particular, the char is oxidized in a fluidized bed, preferably with other carbonaceous materials, and the heat recovered is used, e.g., to dry feed coal.



**EP 0 227 197 A3**



DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
Y	DE-A-2 729 764 (DAVY BAMAG) * Pages 1,2,9-11 *	1	C 10 J 3/54 C 10 J 3/84 C 10 J 3/46
A	---	2-5,8	
Y	US-A-4 508 542 (LANGHOFF) * Column 3, line 56 - column 4, line 44; columns 9-10, claims *	1	
A	--- DE-A-2 918 859 (VEREINIGTE ELEKTRIZITÄTSWERKE WESTFALEN) * Page 12, line 9 - page 14, line 5; page 16, lines 11-17 *	1	
A	--- US-A-2 633 416 (GORNOWSKI) * Column 6, lines 1-21; column 7, line 57 - column 8, line 30 *	5,6	TECHNICAL FIELDS SEARCHED (Int. Cl.4)
A	--- GB-A-2 058 829 (MONSANTO) * Page 2, line 34 - page 3, line 19 *	6	C 10 J
-----			
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 04-11-1987	Examiner WENDLING J.P.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

